



Low-temperature catalytic hydrogenation of silicon and germanium tetrachlorides on the modified nickel chloride



Andrey V. Vorotyntsev^{a,*}, Anton N. Petukhov^a, Ilya V. Vorotyntsev^a,
Tatyana S. Sazanova^a, Maxim M. Trubyanov^a, Irina Yu. Kopersak^a, Evgeny N. Razov^b,
Vladimir M. Vorotyntsev^a

^a Nizhny Novgorod State Technical University n.a. R.E. Alekseev, Nanotechnology and Biotechnology Department, Nizhny Novgorod, 603950, Russian Federation

^b Institute for Problems in Mechanical Engineering, Russian Academy of Sciences, Nizhny Novgorod 603024, Russian Federation

ARTICLE INFO

Article history:

Received 4 April 2016

Received in revised form 1 June 2016

Accepted 4 June 2016

Available online 6 June 2016

Keywords:

Silicon tetrachloride
germanium tetrachloride
catalysis
hydrogenation
nanopowder
silicon
germanium
kinetic
nickel chloride

ABSTRACT

The catalytic reduction of SiCl_4 and GeCl_4 by hydrogen to silicon and germanium nanopowder was carried out over a modified nickel chloride catalyst. The effects of nickel chloride surface on the reaction were intensively investigated. The results show that modified nickel chloride surface play an important role in reduction the value of the activation energy and reaction temperature of the catalytic hydrogenation SiCl_4 and GeCl_4 . Elemental analysis of the catalyst and reaction results demonstrate that the catalyst operates in a temperature range from 423 to 573 K. Further temperature increase above 623 K was impractical as it led to a change in catalyst composition and silicide/germanide is formed in reactor. The resulting knowledge has helped to assume the reaction mechanism which is based on the formation of SiCl_2 and GeCl_2 in the reaction zone. This study will be useful in understanding the reduction of SiCl_4 and GeCl_4 with hydrogen and provides information regarding the development of a SiCl_4 converter for a Siemens reactor to produce poly-Si in the solar cell industry and produce Ge nanopowders with minimum energy consumption.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Nowadays nanotechnology is the recent progress in the manufacture and characterization of low-dimensional nanostructures such as nanowires, nanodots, nanotubes, nanoparticles, etc. made from materials and alloys with unique properties. Nanostructures have been studied and tested in detail nanoelectronic systems and Nanooptics, Nanomechanics and Nanobiology. Formation of Ge nanodots (CT) and nanoparticles crystallographic pristine silicon surfaces have been studied for many years [1,2]. Further studies have focused on the deposition multistructures with built nanoparticles [3]. Dislocations stress and dangling bonds at the interface of the Ge and Si to the different lattice constants can affect the quality of these structures and their changes expected physical behavior [4–6].

* Corresponding author. Nizhny Novgorod State Technical University n.a. R.E. Alekseev, Nanotechnology and Biotechnology Department, Minina st 24, Nizhny Novgorod, 603950.

E-mail address: an.vorotyntsev@gmail.com (A.V. Vorotyntsev).

Silicon tetrachloride is a major byproduct of polycrystalline silicon (poly-Si) production through the chemical vapor deposition (CVD) process of SiHCl_3 [5]. Because a drastic increase in the production capacity of poly-Si in the solar cell industry is expected in the near future, finding an efficient process of converting SiCl_4 to useful products is becoming more and more important environmental and economically, and the reaction of hydrogenation of SiCl_4 has become the focus of recent basic scientific and technological research.

There are several approaches to reducing silicon tetrachloride. The main commercially successful process is silicon tetrachloride processing and reuse through high-temperature reduction in the form of chlorosilanes [7]. There are a number of other, less widespread methods: hydrogenation with the application of highly reactive reductants (for example, metal hydrides) [8], plasma hydrogenation [9] and catalytic reduction [10–18].

All these methods have their own advantages and drawbacks. Their disadvantages include high energy consumption; high production cost; contamination of reaction products with electroactive impurities which is unacceptable in modern microelectronic appli-

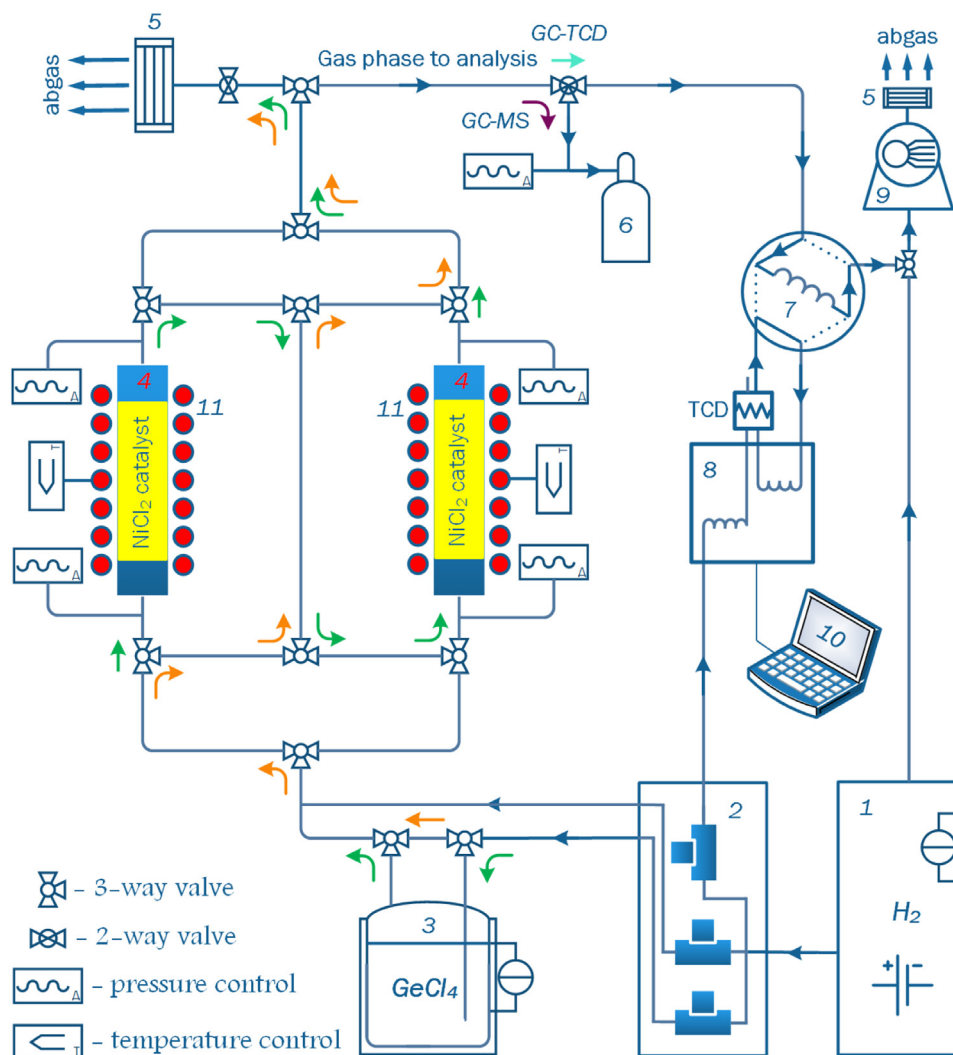


Fig. 1. Apparatus for investigation of the catalytic reduction of silicon/germanium tetrachloride: 1–hydrogen source, 2–mass flow controller, 3–bubbler (tank with $SiCl_4/GeCl_4$), 4–continuous-flow reactor, 5–cartridge filter, 6–GCMS sampler, 7–6-way Swagelok valve, 8–GC analysis (with TCD), 9–vacuum pump, 10–PC; → – operating mode, → – purge mode, → – GCMS analytic line, → – GC analytic line.

cations; necessity of toxic waste disposal; complicated apparatus and low product yield.

Recent years have seen great advances in catalytic reduction processes. The following catalysts are in common use: Ni and Si powders and their mixtures [10,11], copper (I) oxide, copper (I) chloride and iron (II) chloride [10,12,14]. Bulan and Weber [14] reduced silicon tetrachloride in the presence of aluminum, vanadium, and antimony chlorides, bromides and iodides. Koether [15] used copper silicide as a catalyst. Bohmhammel et al. [16] used a niobium, tantalum, or tungsten heating element as a catalyst. Good results were obtained when applying mixtures of Group 2A metals and their salts as catalysts [17]. Qiguo Chen and Wenlong Chen [12] used copper halides mixed with alkali metals as catalysts. Yank et al. [18] proposed applying activated charcoal with a specific surface area above $104 \text{ m}^2/\text{kg}$ as a hydrogenation catalyst support.

Transition metal silicides, formed by the reaction of the metal with $SiCl_4-H_2$ mixtures under hydrogenating reaction conditions, are known to allow a substantial lowering of the reaction temperature of the hydrogenation of $SiCl_4$ as compared to the uncatalyzed reaction [19–22]. Ingle and Peffley reported that copper hydride was an active catalyst which reacted with $SiCl_4$, forming copper chloride and $SiHCl_3$, and the process parameters affecting $SiHCl_3$ yields [23]. Meanwhile, Gusev et al. offered a plasma process, as

well as a catalytic hydrogenation process, coming to the conclusion that pressure in the reaction zone played a key role in determining the $SiHCl_3$ yield of $SiCl_4$ plasma hydrogenation [24,25].

When dealing with transition metals in a catalytic reaction containing chlorine, it is important to note whether the metals are removed from the solid phase in the form of volatile metal chlorides or the silicide catalysts are stable under the reaction conditions. Therefore, Acker and Bohmhammel reported the thermodynamics results of transition metal silicides and suggested that these can be formed in situ by reaction of metal with a $SiCl_4/H_2$ atmosphere [20].

Vorotyntsev et al. [26,27] performed quantum-chemical calculations of the hydrogen reduction of silicon chlorides and theoretically determined the relevant activation parameters. It is of interest to experimentally determine these parameters and compare them with calculation results.

Silicon tetrachloride finds wide application in microelectronic and chemical industries but a large amount of silicon tetrachloride forming in semiconductor silicon production is not used. The reason for this is the following: reduction of silicon tetrachloride requires much energy. In view of semi-conductor silicon production scale-up, the problem of silicon tetrachloride processing and reuse in semi-conductor silicon production is of great practical importance.

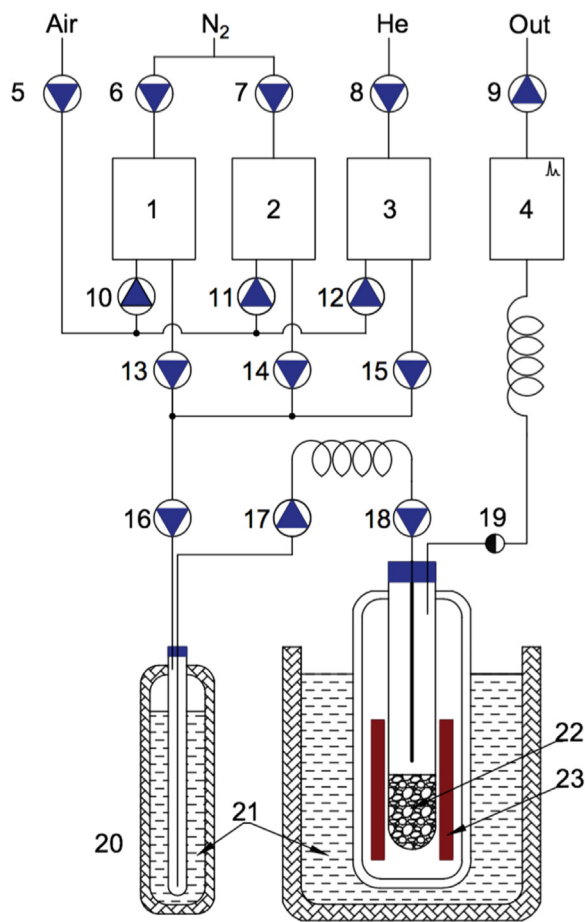


Fig. 2. Apparatus for investigation specific surface area and porosity: 1–3–mass flow meter, 4–TCD, 5–18–needle valve, 19–40 micron filter, 20–cryotrap, 21 – liquid nitrogen, 22–catalyst sample, 23–heater.

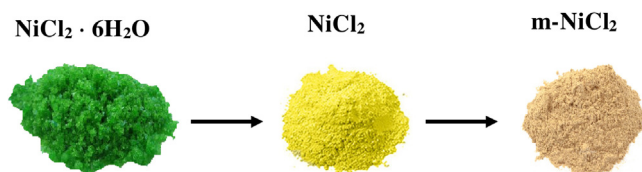


Fig. 3. Pictures of the representative catalysts prefer and after modification.

Thus, in both economic and environmental contexts, all forming silicon tetrachloride should be converted to less energy consuming raw materials that could be used in semiconductor silicon production process with the aim of creating a closed production loop.

At present elementary germanium is the purest substance. Germanium is widely used in micro- and nanoelectronics for fabrication of pulse, parametric and tunnel diodes, microwave converters. It is also applied in IR engineering for fabrication of optical elements: lenses, reflecting mirrors, windows, and lasers. High-purity germanium doped with special impurities retains its dominant position as one of the most promising materials for production of high-sensitivity IR photodetectors. One of the most important practical application areas of high-purity single-crystal germanium is fabrication of ionizing radiation detectors. High-purity germanium, semiconducting germanium layers, germanium dioxide and fiber-optic light-emitting diodes, containing germanium, are produced from its high-purity volatile compounds,

Table 1
Nitrogen physisorption isotherm (77 K) of the modified NiCl_2 .

Catalyst	$S_{\text{BET}}, \text{m}^2 \cdot \text{g}^{-1}$	$V_p, \text{cm}^3 \cdot \text{g}^{-1}$	$d_{\text{BJH}}^{\text{Ads}}, \text{nm}$	$d_{\text{BJH}}^{\text{Des}}, \text{nm}$
m- NiCl_2	312.4	0.62	14.3	9.7

germanium tetrachloride and germanium hydride (monogermane) [28].

The industry widely employs a “chloride” method for obtaining high-purity germanium [29]. The main problem of the chloride technology is low yield of germanium ($\leq 70\%$) and also substantial loss with chloride sewage water and contamination of the final product at the stage of germanium tetrachloride hydrolysis. In addition, chlorides are toxic and corrosion-active substances, which, in turn, makes the “chloride technology” rather labor consuming as regards its instrumentation. Up to 70% of capital expenditure and maintenance expenses are constituted by costs associated with purification of wastewater and effluent gases, as well as appreciation of equipment [30,31].

Monogermane is produced by means of reaction in which germanium tetrachloride is reduced by simple and complex metal hydrides. Germanium oxide and magnesium germanide serve as germanium-containing reagents. Lithium and potassium hydrides, lithium and sodium borohydrides, lithium aluminohydride and diisobutylaluminum hydride [32] in solutions with organic solvents and in the gas phase are used as reducing agents.

All chemical methods for synthesis of hydrides have important shortcomings. First, they are nonselective: hydrides of other elements are simultaneously generated which requires the application of complex and expensive purification techniques [33–35], and the resulting gas contains substantial amounts of by-released hydrogen. Second, the reaction yields a large amount of toxic wastes with which a part of germanium is lost. Third, the process performed in the reactor is difficult to control and monitor and, therefore, a search for other ways to synthesize germanium, based on a research into the mechanisms of reaction products formation, is of particular interest.

In development of new synthesis methods it is necessary to obtain the minimum amount of starting reagents and number of synthesis stages, which makes the reduction of the contamination level [36–38] of the product possible. It seems that the most advantageous in this regard is the direct catalytic reduction of silicon and germanium tetrachloride to give as final products.

Seeing this impressive precedent work has inspired the current study toward the evaluation of the catalytic activity of nickel chloride base catalyst for reduction of silicon and germanium tetrachlorides to nanopowder of silicon and germanium, respectively to reduce the reaction temperature.

2. Experimental

2.1. Apparatus

The apparatus used in the reaction experiment is shown schematically in Fig. 1. It was made of a stainless steel 316SS and various Swagelok ball valves with Dow Corning® 111 Valve Lubricant, resistant to chlorides of silicon, germanium, and hydrogen chloride.

In experiments reactor temperature varied within the range of $423 \div 623 \text{ K}$. Silicon/germanium tetrachloride was delivered into reactor by bubbling hydrogen through a liquid layer of silicon/germanium tetrachloride in the ratio $\text{H}_2/\text{MCl}_4 = 3 \div 15$ (temperature in 3, Fig. 1 was $273 \div 293 \text{ K}$, $M = \text{Si/Ge}$) and hydrogen flow for each ratio rate was 5, 15 and 30 ml/min in order to form kinetic curves. In this work we used silicon/germanium tetrachlo-

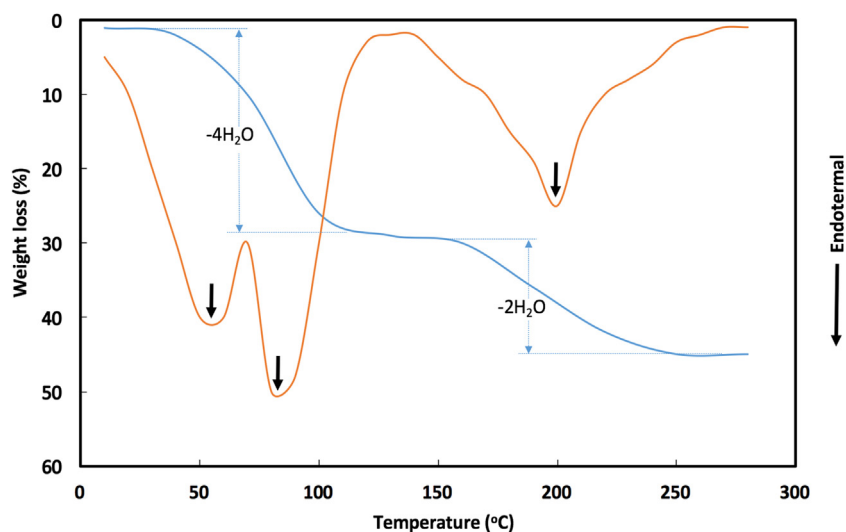


Fig. 4. TGA and DSC curves of nickel chloride hexahydrate.

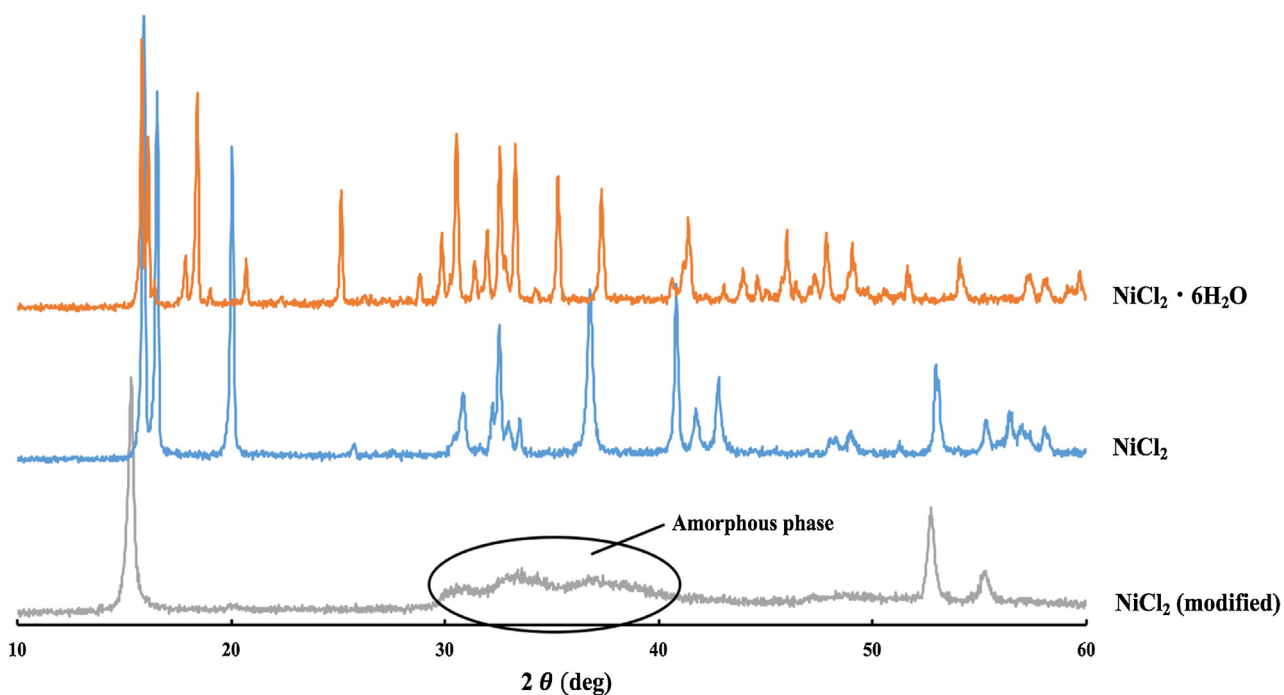


Fig. 5. XRD patterns of a catalyst sample after heating with SiCl_4 .

Table 2

Quantitative characteristics of catalytic reduction reactions with SiCl_4 and GeCl_4 .

Reaction	Conversion (%) [*]		Reaction order	E_a (non catalyst) ($\text{kJ}\cdot\text{mol}^{-1}$)	E_a (NiCl_2) ($\text{kJ}\cdot\text{mol}^{-1}$) [*]	HECl_3 yield (mol. %)
	423 (K)	623 (K)				
(7), E = Si	85.3	99.97	0.040	39.96	2.898	10 – 12
(7), E = Ge	53.1	98.9	0.175	48.49	5.507	–

^{*} RSD (%) = $10 (\text{SiCl}_4)/12 (\text{GeCl}_4)$.

ride 5.0 (99.999%) and hydrogen 6.8 (99.99998%) containing water and oxygen at a level of 0.1 and 15 ppm, respectively.

The sample's specific surface area and porosity were determined by the low temperature nitrogen adsorption using the apparatus shown on Fig. 2.

The gas mixture preparation were made from helium which were use as carrier gas and nitrogen which were used as

gas-adsorbate. The pressure of helium and nitrogen were 0.25–0.05 MPa. The gas mixture flows into liquid nitrogen trap for purification from moisture contamination. Then the it was used *in-situ* by adsorber.

The adsorption and desorption of N_2 was measured at 77 K. Prior to measurement, the sample was kept in vacuum at 193.15 K for 10 h. The linear part of the Brunauer–Emmett–Teller (BET)

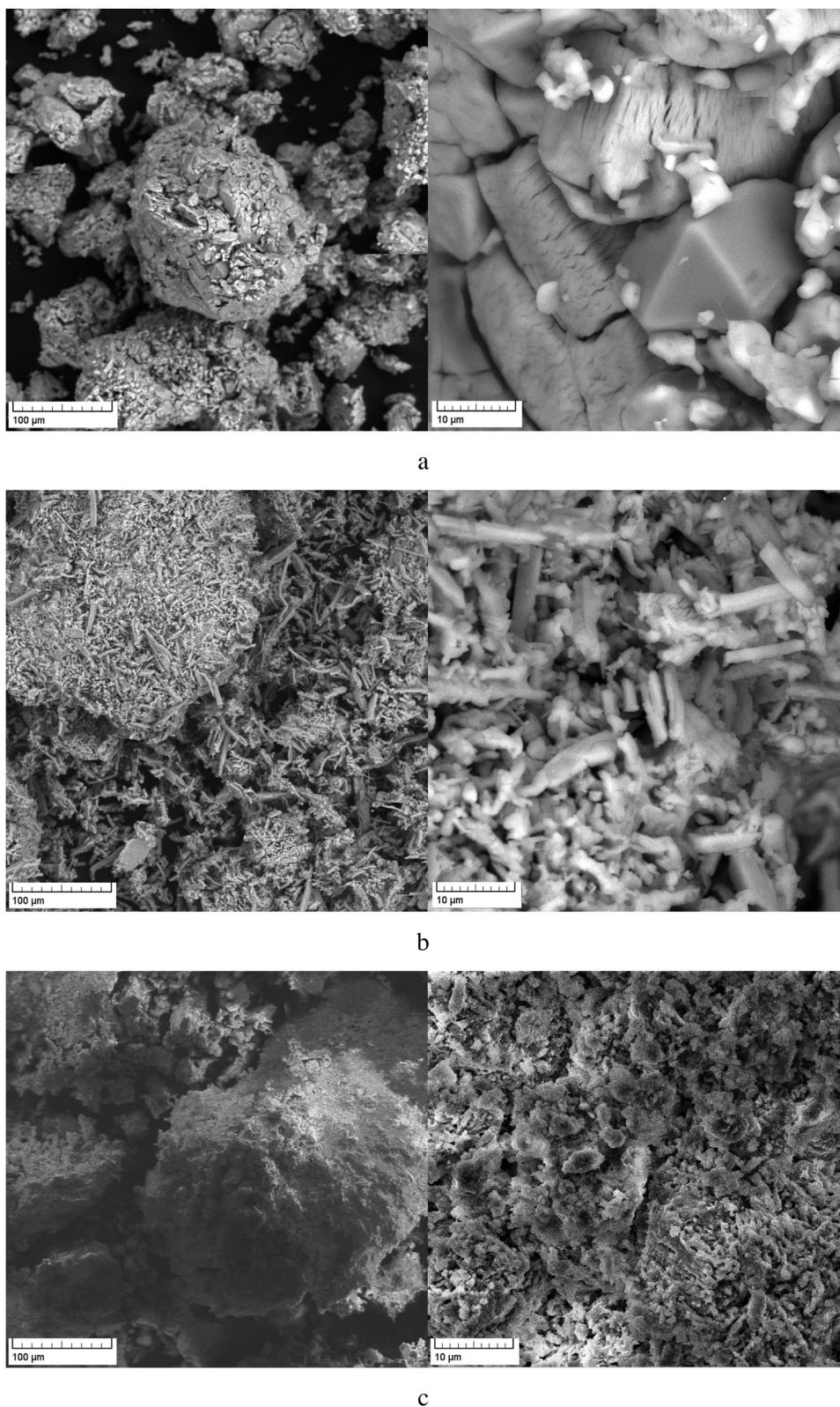


Fig. 6. SEM microphotography of the nickel chloride hexahydrate (a), anhydrous nickel chloride (b) and modified nickel chloride (c).

curve ($p/p_0 = 0.04\text{--}0.39$) was used to calculate the specific surface area. The Barrett-Joyner-Halenda (BJH) formula was used to calculate the pore size distribution based on the adsorption–desorption isotherms of N_2 .

The construction of the absorber allows to carry out the processes of adsorption and desorption. After the gas mixture goes into the thermal conductivity detector (TCD) and then vent-off to the atmosphere by capillary pipe.

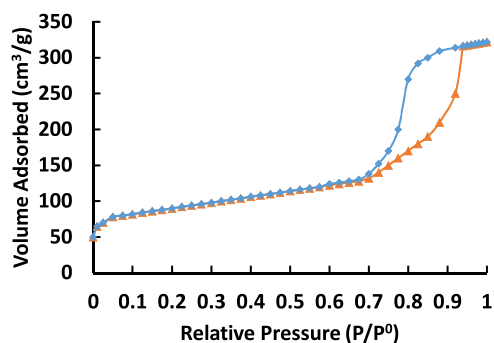


Fig. 7. Nitrogen physisorption isotherms (77 K) of the modified nickel chloride.

The principle of analysis is that during the adsorbate-gas desorption its concentration in gas mixture is increasing with changing of its conductivity which is measured by TCD.

The sorption and desorption isotherms of nitrogen were measured for relative pressure p/p_s 0.05–1 at the temperature 77 K. The specific surface area was calculated according to BET. The volume of mesopores and its size distribution were calculated according to the approach proposed by BJH.

2.2. Products analysis

Quantitative analysis of compounds available from the experiment was carried out by a gas chromatography method on GC «Tsvet-800» (Tsvet, Russia) with the application of a thermal conductivity detector (TCD) with a vacuum sample inlet system. For separating components after synthesis we used a 3 m long packed column with Chromaton N-AW-HMDS (0,16 ÷ 0,20 mm) with 15% applied liquid phase E-301 at 373 K for 6 minutes. The results obtained were processed with «Tsvet – analytic» software. Qualitative analysis of the major reaction products was carried out on gas chromatography-mass spectrometric complex Shimadzu «GCMS – QP2010Plus» (Shimadzu, Japan) with a vacuum sample inlet system through automatic injection valve (Valco Instruments Co Inc, USA) and sampling system (6 Fig. 1). Reaction products were separated on an Agilent capillary column with a stationary phase based on trifluoropropylmethylpolysiloxane at 323 K for 10 minutes; carrier gas – helium 7.0 (99.99999%). Reaction products were identified with the help of NIST-11 database of mass spectra and «GCMS Real Time Analysis» software. Relative standard deviation (RSD) of GC analysis with thermal conductivity detector for concentration was 10% for SiCl_4 (detection limit – 300 ppm) and 12% for GeCl_4 (detection limit – 500 ppm).

For the analysis of intermediates, such as dichlorosilylene/dichlorogermylene, was used a thermal desorption method with a two-stage pyrolyzer EGA/PY-3030D (Frontier Lab) conjugated with chromatography-mass spectrometer Shimadzu GCMS – QP2010Plus. Sample weight of yellow solid substance (previously identified as $(\text{SiCl}_2)_n$ and $(\text{GeCl}_2)_n$) was placed in the melting pot of the pyrolyzer and after that the sample was subjected to two-stage heating. At the 1st stage were removed trace amounts of substances, such as HCl and GeCl_4 in accordance with the following temperature program: 50 – 150 °C (50°/min), holding at 150 °C (5 min). At the 2nd stage the sample was pyrolyzed at 450 °C (10 min). During the second stage identification of resulting chromatographic peaks was carried out with the help of a mass selective detector.

2.3. Catalyst preparation and characterization

In order to carry out reduction of silicon/germanium tetrachloride with hydrogen we used modified nickel chloride as a catalyst.

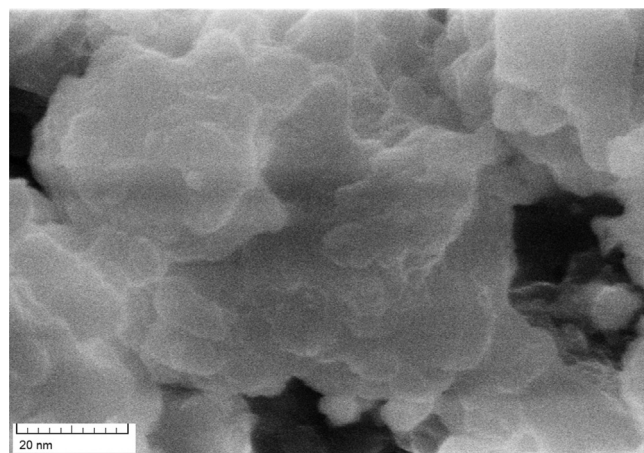
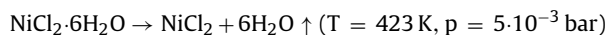
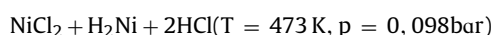


Fig. 8. SEM microphotography of the porous modified nickel chloride.

Nickel (II) chloride hexahydrate (98%, Sigma-Aldrich) was applied as a precursor of a heterogeneous catalyst, based on nickel chloride (II), synthesis. Synthesis of the catalyst was carried out in two stages. At the first step Nickel (II) chloride hexahydrate was dehydrated in a vacuum in accordance with the temperature program: 50 – 300 °C (10°/min) and holding at 300 °C (6 hours).



After that resulting yellow crystals of nickel chloride (II) were placed in a vacuum cup made of tungsten carbide and milled in planetary ball mill Retsch PM100. Ball-to-powder weight ratio: 10:2; ball diameter: 16 mm; speed: 250 RPM. The Nickel (II) chloride powder was milled up to 10 h to reach steady state condition. Then nanopowder of nickel chloride was placed in reactor 4 (Fig. 1) and heated with hydrogen and hydrogen chloride (99.99%) in the ratio $\text{HCl}/\text{H}_2 = 1,5$ at the temperature of 473 K for 1.5 hours. Catalyst surface was etched to increase the number of active sites of the catalyst. As a result, reductive-oxidative reactions took place:



Consequently, nickel chloride changed its color from yellow to orange (Fig. 3).

Analysis of the all catalyst samples before and after modification, silicon and germanium nanopowders was performed on X-ray diffractometer Shimadzu XRD-7000. The measurements were made at 40 kV and 30 mA. The installed DS and SS of scattering slit correspond to angular divergence of incident and diffracted beams equal to 1°. The scattering slit RS front of the detector has a width of 0.3 mm. The exposure we saved in the range of angles 10° ÷ 60° (2θ). Step scan was 0.02°, the exposure at each step was 0.5 sec. Quantification analysis was made by programing complex EVA with help of data base PDF-2 2012. Phases search were made by assign the chemical filter Si, Ge, Cl, O, H, Ni.

Microrelief The SEM images were taken with Tescan Vega II electron microscope at the voltage of 20 kV with backscattered electron (BSE) detector and detector of reflected electrons (RE detector) with zooming from 500 to 8000 and 20000. The use of BSE and RE detectors allows to obtained the most contrast images in comparison with SE detector. Moreover the BSE detector is allows to conduct the elementary analysis of the surface based on the dependence of molecular weight of element from the brightness of the surface. More bright part of the image corresponds to the presence of more heavy elements there.

For thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) measurements, samples between 5 and 8 mg were placed in open alumina pans and experiments were

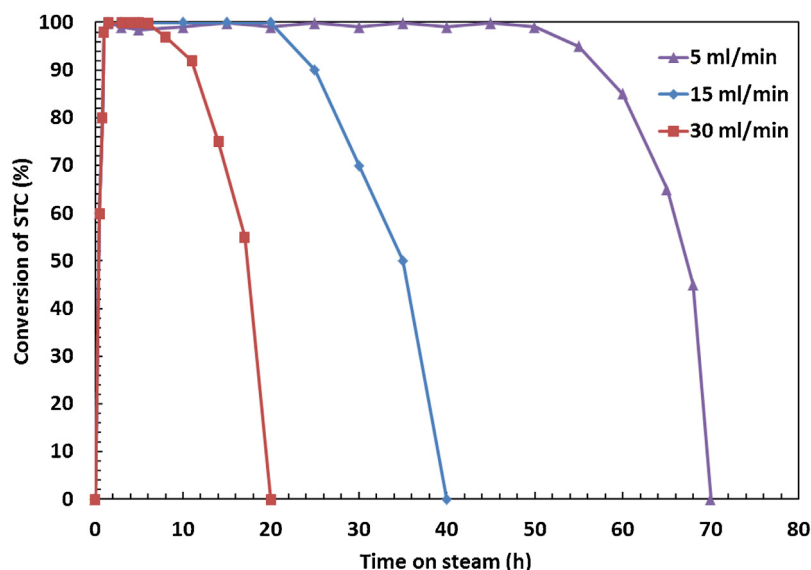
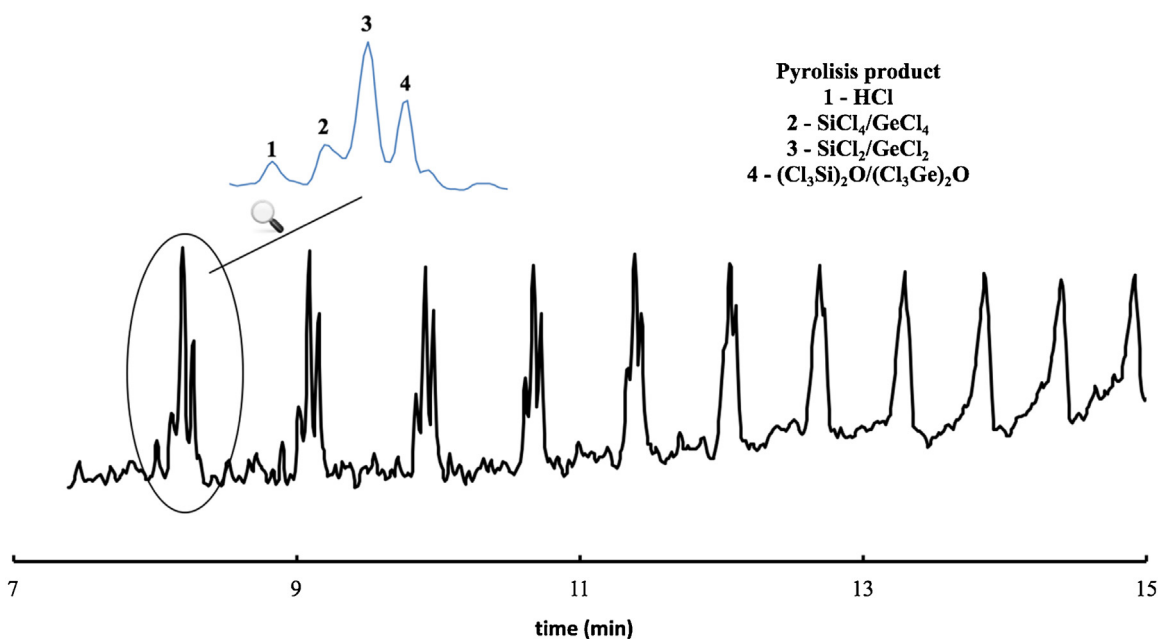


Fig. 9. Conversion of STC in stream.

Fig. 10. Chromatogram of the sample (SiCl₂)_n after pyrolysis (chromatogram of (GeCl₄)_n looks like similar, but there is a shift of delay time for 2.12 min).

conducted using STA 449 F1 Jupiter (NETSCH, Germany) thermal analyzer. The thermograms were recorded from 50 to 350 °C temperature range and with 10 °C/min in an atmosphere of argon.

3. Results and discussion

3.1. Catalyst characterization

A number of processes are carried out at elevated temperatures, thus it is necessary to study the catalyst material thermal properties. The thermal properties of the obtained films are shown in the gravimetric analysis (TGA) and differential scanning calorimetry (DSC) diagrams presented on Figs. 4.

From TG analysis of NiCl₂ · 6H₂O, presented in Fig. 4 shows that dissociation of crystalline occurs in two main steps, first in the temperature range of 24 – 120 °C. There is a loss of four water molecules (which corresponds to a weight loss of 30%). Complete

dehydration obtained dihydrate to anhydrous NiCl₂ takes place above 250 °C, which loss of two water molecules in the temperature range 110–250 °C (which corresponds to 15%). Total sample of catalyst lost 45% of weight, in good agreement with the calculated value (45.48%)

DSC curve (Fig. 4) of NiCl₂ · 6H₂O shows three endothermic peaks. First and second peak coincides with the first step of dehydration of crystalline on the TGA curve (peak 1 corresponds to the loss of two molecules of water, with consequent loss of the type two water molecules). Third endothermic peak coincides with the second step of the TGA curve with the loss of last two water molecules.

At each stage, nickel chloride modifications have been XRD studies performed. Measured diffraction pattern (Fig. 5) shows that after treating chloride nickel in phases composition appear amorphous phases which have the strongest catalytic effect on the reaction. During experiments it was found that the catalyst of this nominal

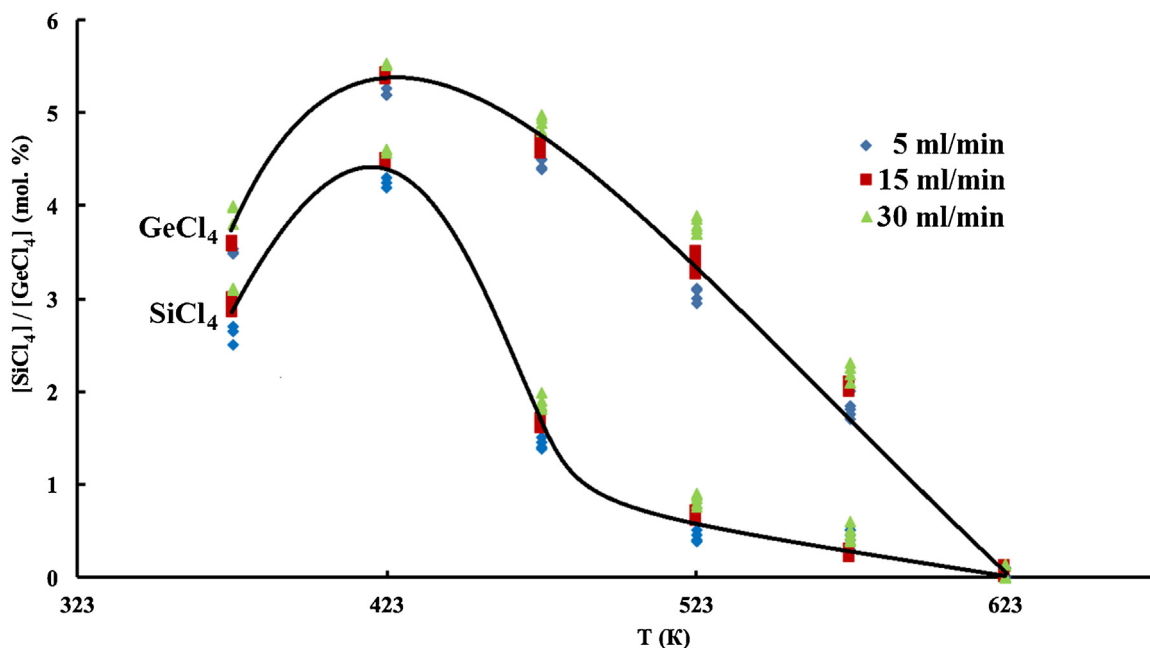


Fig. 11. Concentration change of SiCl_4 and GeCl_4 in the temperature range 324–623 K.

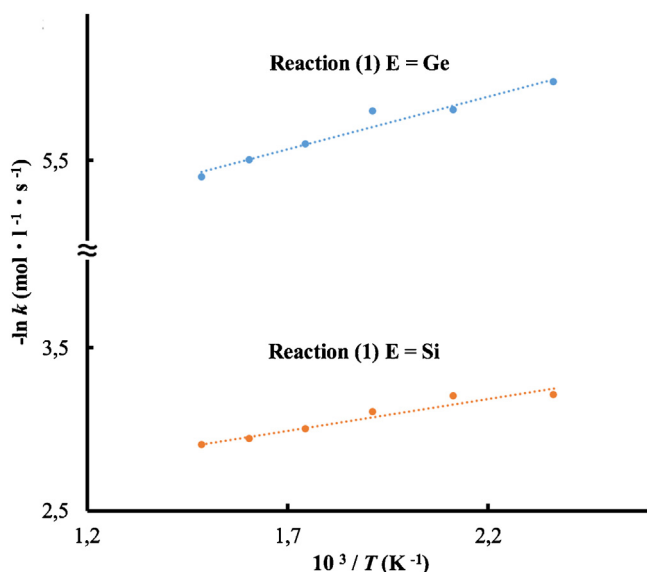


Fig. 12. Arrhenius plot of the reaction rate: the points represent the experimental data and the line represents a least squares fit (trend line).

composition has the highest catalytic properties unlike anhydrous nickel chloride.

Fig. 6 presented SEM microphotography of the nickel chloride hexahydrate (a), anhydrous nickel chloride (b) and modified nickel chloride (c), after heated with hydrogen and hydrogen chloride. The conclusion that the treatment of nickel chloride by gas mixture of hydrogen and hydrogen chloride leads to increasing of specific surface area made base on obtained SEM-images and X-ray scattering (XRD results). Such treatment is decreasing of particles size because of etching as shown on Fig. 6c. This enlarging of specific surface gives to modified nickel chloride more catalytic activity. Moreover, structure of the catalyst is also changed and being more porous and layers like form.

As evidenced by Fig. 7 the resulting modified nickel chloride show hysteresis in relative pressure range 0,7–0,9 (type IV a). This

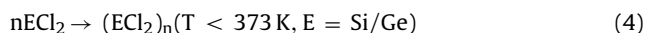
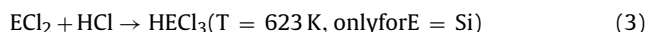
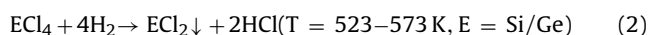
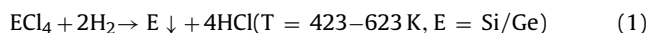
behavior is characteristic for mesoporous materials with a narrow pore size distribution with maximum absorption due to capillary condensation.

According Fig. 8, structure must have ink-bottle as pores which induced by the particles induced of NiCl_2 and formation agglomerates during their production and modification. The specific surface characteristics are presented in Table 1.

There are two main categories of pore sizes, first near 14 nm and it has been connected by windows with a size 10 nm. In addition, the nanoporous character of modified NiCl_2 shown by SEM microphotography (fig. 8).

3.2. Experimental catalyst hydrogenation kinetic properties

The chromatograms and mass spectra of the main products formed in the reaction of silicon/germanium tetrachloride reduction, obtained in the study, indicate that the following reactions occur when the process is performed:



As a part of the study reduction of silicon/germanium tetrachloride with hydrogen in the presence of catalyst based on modified nickel chloride (II) was carried out. It was found that the reaction (1) takes place with a high degree of conversion at 623 K (Table 2), and that the reaction (2) is a side reaction and leads to the formation of silicon/germanium dichlorides which are polymerized in $(\text{ECl}_2)_n$.

With reference to Fig. 18, the nanopowder of Si has narrower PSD than the nanopowder of Ge. Additionally Si has less average particle size than Ge.

Thus the observed high value of conversion is related to rapid takeout of HCl from the reaction zone and to high dilution of initial gas mixture by hydrogen (the dilution ratio as follows: MCl_4 :

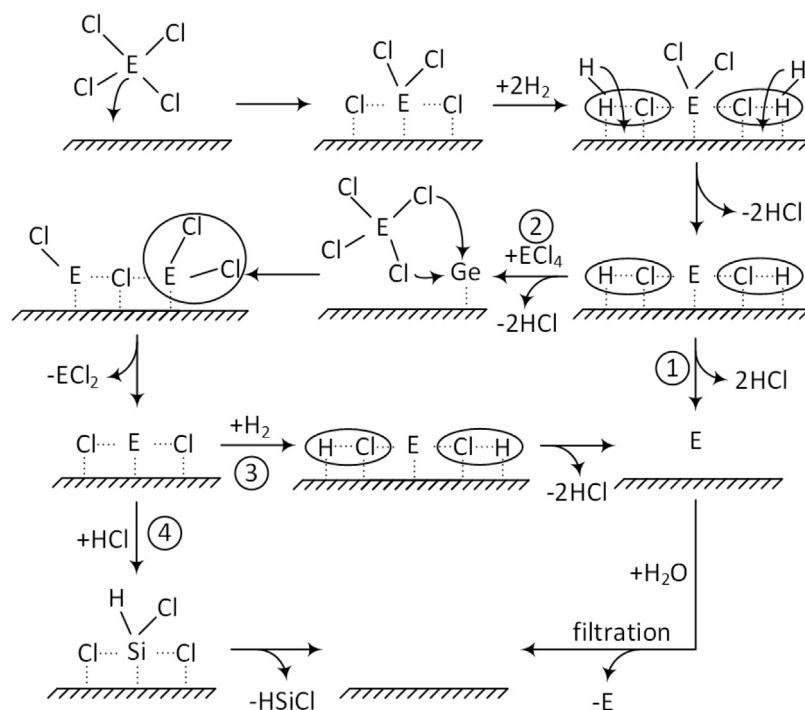


Fig. 13. Mechanism of the reaction Si/GeCl₄ on the surface.

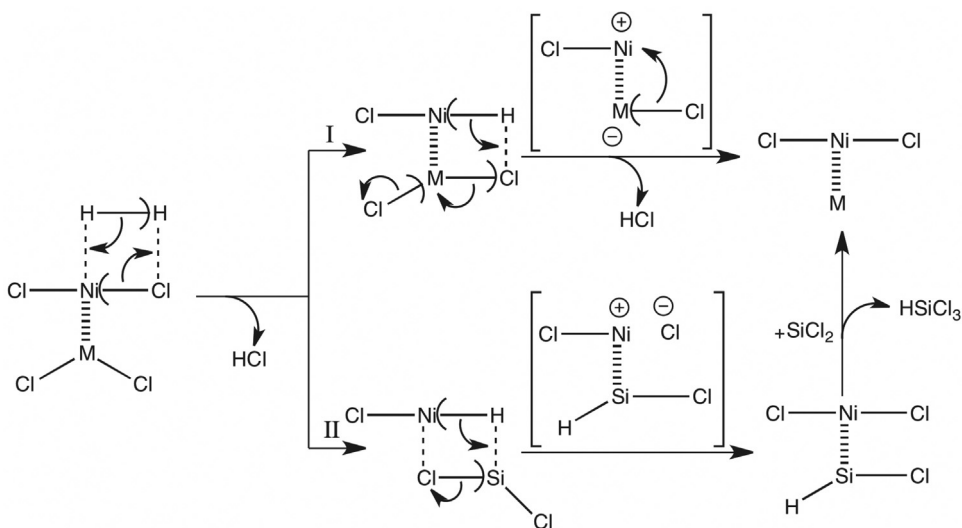


Fig. 14. Mechanism of the reaction Si/GeCl₄ on modified nickel chloride surface with different coordination.

H₂ = from 1: 2 to 1: 14 (M = Si/Ge). This helps to keep the high process rate during the required time as well as shifts the equilibrium to the formation of the target product.

As seen from Fig. 9 in the reaction there is an induction period of ~1 hour, then the conversion is maintained at 99%, but after 70 hours the catalyst activity decreases due to closure of the active centers of the nickel chloride catalyst because of formation of germanium/silicon. Catalyst deactivation occurs earlier in the case of increasing the volume tetrachloride in the mixture, which is evident from Fig. 9. This fact shows that it requires further separation or conversion into trichlorosilane by hydrochlorination reaction of silicon. For this purpose, the experimental set up has two reactors (Fig. 1) which facilitate stepwise decomposition of silicon tetrachloride and trichlorosilane synthesis.

Further temperature increase above 623 K was impractical as it led to a change in catalyst composition: nickel chloride (II) reduced to metallic nickel followed by formation of nickel silicides/germanides [19–21] which exhibit less activity for this reaction. Nickel silicide formation reduces to decrease the reactivity of the catalyst.

It is also worth noting that during the chemical reaction dichlorosilylene/-germylene is formed. In case of silicon tetrachloride it reacts with hydrogen chloride and forms trichlorosilane which yield becomes stable at 673 K and amounts to 10–12% of SiHCl₃. At temperature exceeding the above trichlorosilane is not formed due to degradation or recombination of dichlorosilane. However, in case of germanium tetrachloride trichlorogermane is not detected, supposedly, due to high stability of dichlorogermylene in investigated temperature intervals.

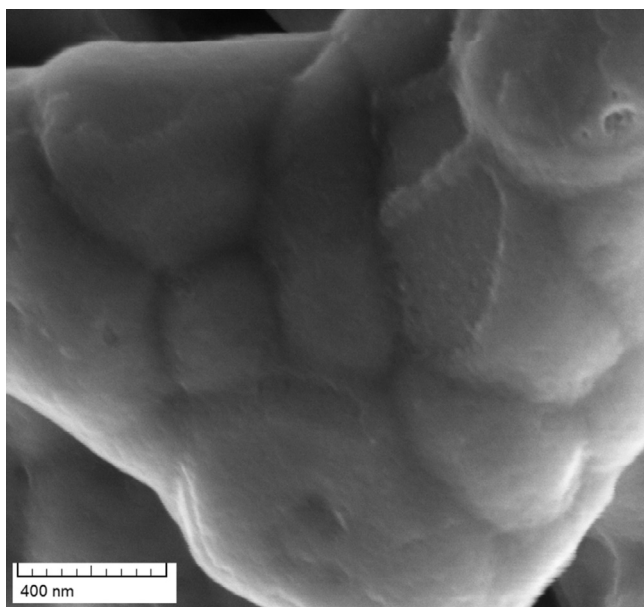


Fig. 15. SEM microphotography of the agglomerating silicon nanoparticles.

Formation of dichlorosilylene/-germylene was discovered by pyrolysis gas chromatography-mass spectrometry, the main products after gently pyrolysis are shown in Fig. 10. Pyrolysis of a sample takes place gradually. At the beginning of desorption of hydrogen chloride, silicon/germanium tetrachloride (Fig. 10 (1) and (2)) and hexachlorodisiloxane can be observed which appears as a result of reaction between silicon tetrachloride and oxygen in the carrier gas or interaction with the stationary phase of a capillary column. Concentration of hydrogen chloride, silicon tetrachloride and hexachlorodisiloxane decreases in due course and after 13 minutes the products of pyrolysis contain dichlorosilylene/dihlorogermylene only, which confirms the fact that the analyte is a polymeric structure of general formula $(\text{SiCl}_2)_n$, and 1,2,4 substances in the chromatogram are adsorbed impurities.

Study of kinetic characteristics of the catalytic reduction reaction of silicon/germanium tetrachloride was carried out in a temperature range 423–673 K. Concentration of silicon and germanium tetrachloride remains constant at different flow rates (5, 15, 30 ml/min), and a fold change in the height (from 0.05 to 0.20 m) of the catalyst bed does not change the composition of the gas mixture [39].

According to the results of a gas-chromatographic analysis, a thermal conductivity detector showed kinetic curves of the reaction under study, allowing experimentally determining the dependence of germanium tetrachloride concentration in the gas

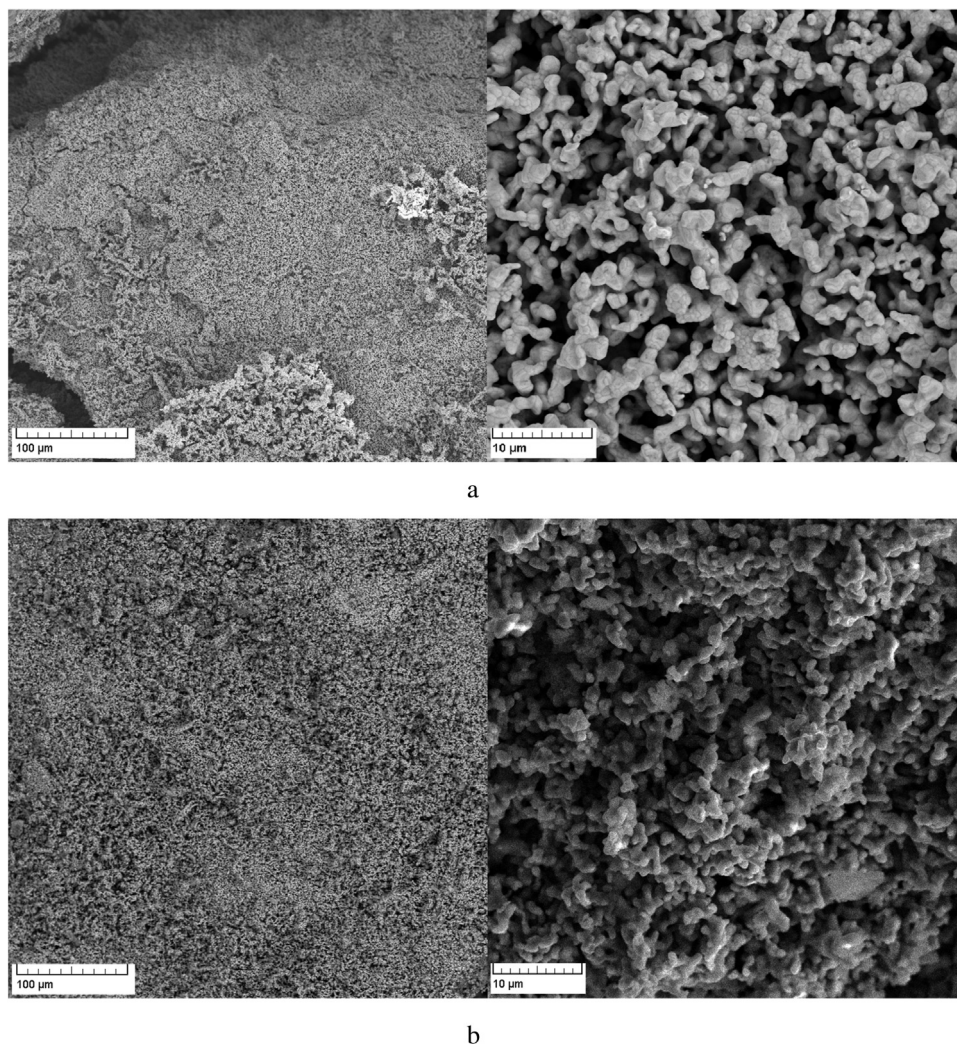


Fig. 16. SEM microphotography of silicon (a) and germanium (b) nanopowders.

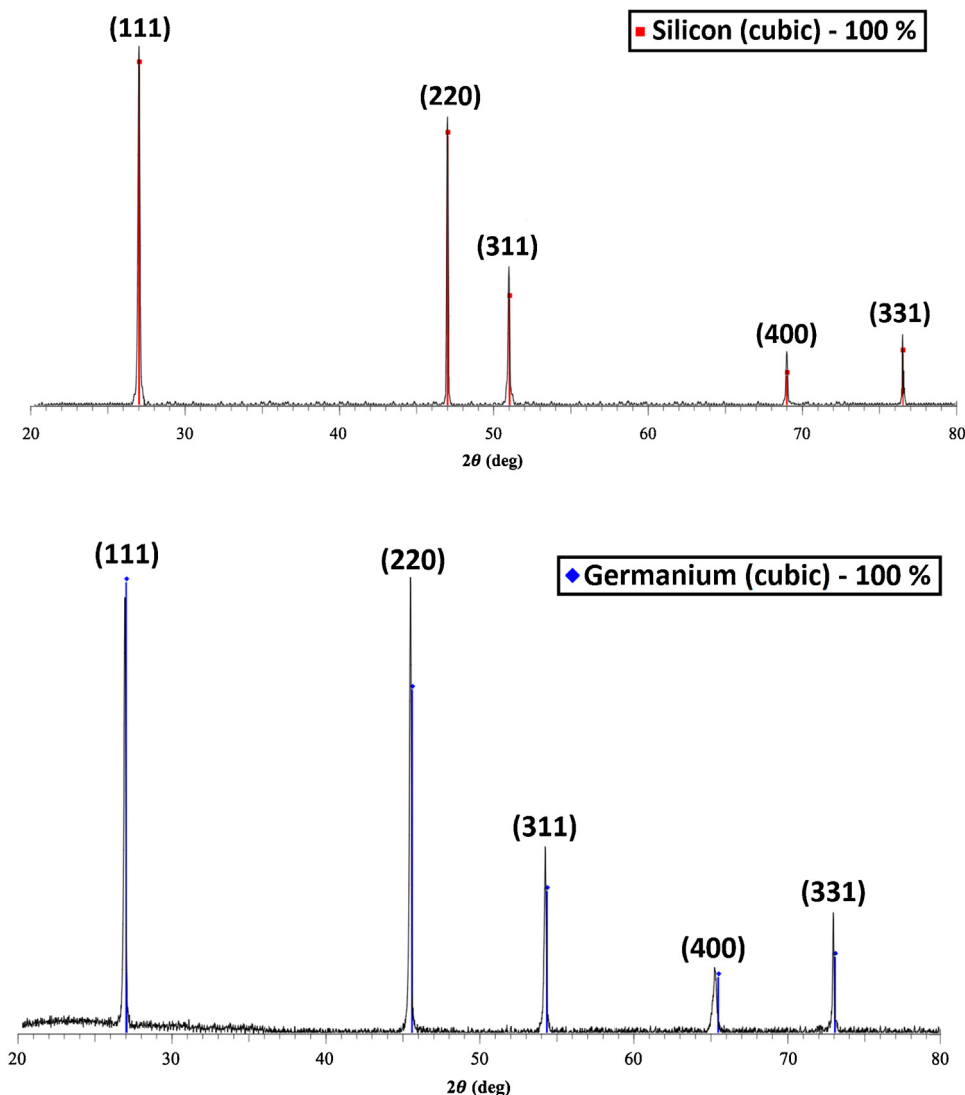


Fig. 17. XRD patterns of the synthesized silicon and germanium.

mixture on reactor temperature at various initial concentrations of germanium tetrachloride (Fig. 11).

The increase of concentrations shown on Fig. 11 is observed due to the fact that the process starts at room temperature and the catalyst is being saturated with the reaction mixture, in particular, at this temperature the adsorption of silicon tetrachloride occurs. Maximum values in the area of 423 K are observed due to the maximum value of thermal desorption of silicon tetrachloride. It is worth mentioning that the area below 150 °C was not taken into account for the calculation of the activation energy.

On the ground of the obtained data we developed a logarithmic dependence of the reaction rate on the concentration, which is described by the equation:

$$\ln V = (0.040 \pm 0.0002) \ln C - (6.984 \pm 0.045) \text{ (for SiCl}_4\text{)} \quad (5)$$

$$\ln V = (0.175 \pm 0.0004) \ln C - (0.357 \pm 0.009) \text{ (for GeCl}_4\text{)} \quad (6)$$

where V – rate of the chemical reaction ($\text{mol} \cdot \text{l}^{-1} \cdot \text{s}^{-1}$) and C – concentration of silicon/germanium tetrachloride ($\text{mol} \cdot \text{l}^{-1}$).

From the slope of the relevant plot the order of reaction was found to be near zero (0.04 and 0.175). This means that large amounts of reactants were adsorbed on the catalyst. Thus, reaction rate almost did not depend on reactant concentration in the vapor phase, as the rate of reactant indiffusion to the active center

of the catalyst considerably exceeded the rate of the active center emptying after the chemical reaction. Moreover, varying the flow rate of the silicon tetrachloride vapor – hydrogen mixture at the reactor inlet and the thickness of the catalyst layer (from 0.05 to 0.20 m) had no effect on the gas–vapor mixture composition, which also suggests that the reaction proceeds in the kinetic region and diffusion is not rate-limiting step.

The present experimental data were used to evaluate the rate constant as a function of temperature. The corresponding Arrhenius plot was linear (Fig. 12). Least squares fitting of the data yielded an equation for the temperature-dependent rate constant of reaction (1):

By processing the data by the least-squares method, we obtained an equation for determining the rate constant of the chemical reaction (7) and (8):

$$\ln k = (2.954 \pm 0.001) - (348.555 \pm 0.105) \times 10^3 / T \quad (7)$$

$$\ln k = (4.598 \pm 0.001) - (662.351 \pm 0.198) \times 10^3 / T \quad (8)$$

From the slope of the Arrhenius plot (Fig. 12), the apparent activation energy of the process was determined to be $E_a = 2.898 \pm 0.171 \text{ kJ} \cdot \text{mol}^{-1}$ for reaction (1, $E = \text{Si}$); $E_a = 5.507 \pm 0.171 \text{ kJ} \cdot \text{mol}^{-1}$ for reaction (1, $E = \text{Ge}$).

3.3. Reaction mechanism

These values are typical of the activation reaction leading to formation of hydrogen chloride, in [40,41] was found activation energy for reaction $\cdot\text{SiCl}_3 + \cdot\text{H} \rightarrow \cdot\text{SiCl}_2 + \text{HCl}$ ($2.5 \text{ kJ}\cdot\text{mol}^{-1}$). Presumably, the limiting step of the reaction is the formation of hydrogen chloride on the catalyst surface. On the ground of data and analysis of researches into this area, a probable mechanism of the reaction has been proposed (Fig. 13).

An important aspect is that reduction reactions of chlorides of silicon and germanium have alternative ways: (Fig. 13 way 1 and 2), which can have both a smaller and a larger contribution under different conditions (ratio of H_2/ECl_4 , temperature and pressure in the reaction zone). These studies have been conducted in many works devoted to processing of silicon and germanium tetrachloride. However, the fact that in identical conditions reduction reaction of silicon and germanium can proceed differently (Fig. 13 way 3 and 4), was discovered for the first time. Moreover as shown on Fig. 10, the significant decreasing of silicon tetrachloride concentration is observing at 473 K, but there is no such behavior for germanium tetrachloride. This concentration loss for silicon tetrachloride is realized because of synthesis of the secondary product which is trichlorosilane and it is evidence of alternative way of the reaction presented (Fig. 13 way 2).

Also the nickel chloride is electron shuttle in electrochemical reaction, consequently we can assume that on its surface the chlorine exchange in between molecules of $\text{SiCl}_2/\text{GeCl}_2$ and hydrogen (Fig. 14). As a result of not similar coordination of $\text{SiCl}_2/\text{GeCl}_2$ molecules, the different transformations might be present with the different products formation, primary silicon or secondary trichlorosilane.

Moreover XRD results shown the presence in catalyst after the process nickel hydride ($\text{NiH}_{0.6}$) with concentration around 0.7% (2θ : 42° , 49° , 72°), which is also evidence of possibility of proposed mechanism of this reaction (Fig. 13)

3.4. Extraction and characterization of silicon and germanium nanopowders

After studying, reaction kinetics catalyst was dissolved in water from MilliporeDirect-Q3 water purification system with resistivity $28.7 \text{ M}\Omega\cdot\text{cm}$ to NiCl_2 solution, separated by centrifugation from solution and filtered with paper filter MACHEREY-NAGEL 1670 (density 85 g/m^2). During filtration silicon and germanium powder settled on the filter. Nanopowders of silicon and germanium were washed and heated for remove traces of water at 110°C in vacuum. SEM images of nanopowders are presented in Figs. 15 and 16, it is seen that in the process of extracting the particles was agglomerating and clear boundaries are visible on the silicon nanoparticles, for example (Fig. 15).

The structure of cover layers presented on Figs. 16 has a textured globular-block surface with the size of separate globules up to 500 nm. Inside the globules we found the presence of the structure formed from smaller globules. Analyzing the morphology of the bigger globules top layer surface we can conclude that during the catalytic hydrogenation the smaller globules is formed. This microstructure looks like nanosized globular structure.

Measured diffraction pattern (Fig. 17) shows that after catalytic hydrogen reduction of silicon and germanium tetrachloride we got nanopowders of silicon and germanium (without nickel or nickel silicides) with single crystalline cubic phase Si and Ge.

SEM micrographs of the surface of the nanopowders of silicon and germanium are shown in Fig. 16. It is apparent that the particles of silicon and germanium form is irregular agglomerates. Particle boundaries are seen plainly on the surface of agglomerates. The

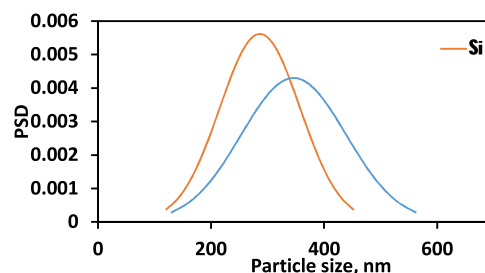


Fig. 18. Particle sizes distribution (PSD).

particles of silicon and germanium have a regular cubic coarse-crystalline structure.

A maximum linear particle sizes were measured for the both nanopowders (sample volume is 100). Samples were analyzed by methods of mathematical statistics, and graphs of particle sizes distribution (PSD) were constructed (Fig. 18).

A statistical analysis was performed in the following way. An intervallic ordered sample was formed from a range of values. An optimum quantity of intervals k was measured by Sturges' formula:

$$k = \log_2 n + 1 \quad (9)$$

where n is sample volume. Then a volume of values falling into each interval was counted, and a histogram was constructed. An asymmetry ratio was measured for a histogram, and an asymmetry type was found. The asymmetry was not large in both cases. For that reason, it is possible that PSD of Si and Ge fits into normal distribution (ND).

The hypothesis about ND was tested by Pearson criterion (or chi-squared test, χ^2) for a significance point of 0.05. The chi-square test uses as its criterion the sum, over predefined groups, of the squared difference between the increases of the empirical distribution and the estimated distribution, weighted by the increase in the estimate for that group. This criterion is one of most faithful criterions. Accept or reject the null hypothesis that the observed frequency distribution is different from the theoretical distribution based on whether the test statistic exceeds the critical value of χ^2 . If the test statistic does not exceed the critical value of χ^2 , the null hypothesis can be accepted with the significance level of confidence. The critical value was 9.4877 in both cases. The test statistic of Si was 0.3310, and the test statistic of Ge was 0.9596. This means that PSD of Si and Ge fits into ND with a significance point of 0.05.

4. Conclusions

In the presented work developed a method of catalytic reduction of silicon and germanium tetrachloride with hydrogen, which lowers the temperature of the process from 1273 to 523 K (SiCl_4) and from 1073 K to 623 K (GeCl_4) with a high degree of conversion. This work will be useful to understanding the reduction of SiCl_4 and GeCl_4 with hydrogen and provides information regarding the development of a SiCl_4 converter for a Siemens reactor to produce poly-Si in the solar cell industry and produce Ge nanopowders with minimum energy consumption compared with analogues.

The catalytic reduction of SiCl_4 and GeCl_4 by hydrogen to silicon and germanium nanopowders was carried out over a modified nickel chloride catalyst. The effects of nickel chloride surface on the reaction were intensively investigated. Measured diffraction shows that after treating chloride nickel in phases composition appear amorphous phases which have the strongest catalytic effect on the reaction. The thermogravimetric analysis and differential scanning calorimetry was used determining the stability of nickel chloride hexahydrate for difention dehydration treatment, because traces of water and oxygen have impair work of catalyst. Specific surface area

and porosity were determined by the low temperature nitrogen adsorption Catalyst is a mesoporous materials with a narrow pore size distribution. Structure must have ink-bottle as pores which induced by the particles induced of NiCl_2 and formation agglomerates during their production and modification. The specific surface was $312.4 \text{ m}^2 \cdot \text{g}^{-1}$ with 10–14 nm pores.

The kinetics of catalytic and non-catalytic reaction was studied. Activation energy of non-catalyst reaction was $39.96 \text{ (kJ} \cdot \text{mol}^{-1})$ for SiCl_4 and $48.49 \text{ (kJ} \cdot \text{mol}^{-1})$ for GeCl_4 . Introducing catalyst into the reaction zone greatly reduces the value of the activation energy to $2.898 \text{ (kJ} \cdot \text{mol}^{-1})$ for SiCl_4 and $5.507 \text{ (kJ} \cdot \text{mol}^{-1})$ for GeCl_4 , shown that there is no diffusion hindrance. Moreover established that the catalyst operates in a temperature range from 423 to 573 K. Further temperature increase above 623 K was impractical as it led to a change in catalyst composition and silicide/germanide is formed in reactor which exhibit less activity for reaction of catalytic reduction. The enhanced SiHCl_3 yield of SiCl_4 hydrogenation in the presence of silicide in temperature 673 K. However, in case of germanium tetrachloride trichlorgermane is not detected, supposedly, due to high stability of dichlorogermylene in investigated temperature intervals. Formation of dichlorosilylene-/germylene was discovered by pyrolysis gas chromatography-mass spectrometry. The resulting knowledge has helped to assume the reaction mechanism which is based on the formation of SiCl_2 and GeCl_2 in the reaction zone. On the ground of data and analysis of researches into this area, a probable mechanism of the reaction has been proposed.

In this paper were obtained nanopowders of silicon and germanium. The structure has a textured globular-block surface with the size of separate globules up to 500 nm. The particles of silicon and germanium form is irregular agglomerates Measured diffraction pattern shows that after catalytic hydrogen reduction of silicon and germanium tetrachloride we got nanopowders of silicon and germanium with single crystalline cubic phase Si and Ge. A maximum linear particle sizes were measured for the both nanopowders. Samples were analyzed by methods of mathematical statistics, and graphs of particle sizes distribution (PSD) were constructed. The nanopowder of Si has narrower PSD than the nanopowder of Ge. Additionally Si has less average particle size than Ge.

Acknowledgments

This work was financially supported by the Ministry of Education and Science of the Russian Federation in the Framework of the Basic Part of the State Task, Project No. 2897. Germanium nanopowder preparation work was financially supported by Russian Science Foundation, project 15-19-00147. Silicon tetrachloride hydrogenation and kinetics was financially supported by RFBR project 16-38-60192 mol.a.dk and 15-48-02703.

References

- [1] B. Voigtländer, M. Kawamura, N. Paul, V. Cherepanov, *J. Phys.: Condens. Matter* 16 (2004) 1535–1551.
- [2] K.N.A. Romanyuk, A. Shklyayev, B.Z. Olshanetsky, A.V. Latyshev, *Pisma v Zh Eksp. Teoret. Fiz.* 93 (2011) 661–666, in Russian.
- [3] T.V. Torchynska, Yu. V. Vorobiev, *Nanocrystals and Quantum dots of group IV semiconductors*, ASP, Stevenson Ranch, USA, 2010.
- [4] D.J. Eaglesham, M. Cerullo, *Phys. Rev. Lett.* 64 (1990) 1943–1947.
- [5] A.V. Gusev, R.A. Kornev, A.Y. Sukhanov, *Inorganic Materials* 42 (2006) 1023–1026.
- [6] J.Y. Leea, W.H. Leea, Y.-Ki Parka, Hee Y. Kima, Na Y. Kanga, K.B. Yoonb, W.C. Choia, O-Bong Yangc, *Catalytic conversion of silicon tetrachloride to trichlorosilane for a poly-Si process*, *Sol. Energ. Mat. Sol.* 105 (2012) 142–147.
- [7] U.S. Patent 4217334, Process for the production of chlorosilanes 1980.
- [8] P.A. Taylor, *AT Purification Techniques and Analytical Methods for Gaseous and Metallic Impurities in High Purity Silane*, *J. Cryst. Growth* 89 (1988) 28–38.
- [9] U.S. Patent 4309259, High pressure plasma hydrogenation of silicon tetrachloride, 1988.
- [10] CN. Patent 2547719, Apparatus for producing trichloro hydrosilicon by hydrogenation of silicon tetrachloride, 2003.
- [11] CN. Patent 101618874 Method for producing trichlorosilane by coldly hydrogenating silicon tetrachloride 2010.
- [12] CN. Patent 101759189 Method for preparing trichlorosilane 2010.
- [13] CN. Patent 101816946 Preparation method and application of catalyst used in hydrogenation of silicon tetrachloride 2010.
- [14] U.S. Patent Application 20040028593, Method for producing trichlorosilane, 2004.
- [15] S. Koether, *Reaktionen im System Metall–Silicium–Chlor–Wasserstoff unter dem Gesichtspunkt der heterogenen Katalyse*, Dissertation zur Erlangung des akademischen Grades, Freiberg (2007).
- [16] U.S. Patent Application 20070173671, Partial pressure swing adsorption system for providing hydrogen to a vehicle fuel cell, 2007.
- [17] Wei-Jie Ding, Zhi-Bo Wang, Jian-Min Yan, Wen-De Xiao, *CuCl-Catalyzed Hydrogenation of Silicon Tetrachloride in the Presence of Silicon: Mechanism and Kinetic Modeling*, *Ind. Eng. Chem. Res.* 53 (2014) 16725–16735.
- [18] Wei-Jie Ding, Jian-Min Yan, Wen-De Xiao, *Hydrogenation of Silicon Tetrachloride in the Presence of Silicon: Thermodynamic and Experimental Investigation*, *Ind. Eng. Chem. Res.* 53 (27) (2014) 10943–10953.
- [19] J. Acker, K. Bohmhammel, *Reactivity of intermetallic compounds: a solid state approach to direct reactions of silicon*, *J. Phys. Chem. B* 106 (2002) 5105–5117.
- [20] J. Acker, I. Roßner, R. Otto, G. Roewer, K. Bohmhammel, *Formation of transition metal silicides by solid-gas reactions: thermodynamic and kinetic consideration*, *Solid State Ion.* 142 (2001) 583–591.
- [21] K. Bohmhammel, G. Roewer, H. Walter, *Hydrodehalogenation of chlorosilanes in the presence of metal silicides: experimental studies of gas and solid phase composition related to thermodynamic calculations*, *J. Chem. Soc. Faraday Trans.* 91 (1995) 3879–3882.
- [22] W. Morke, F. Vogt, K.-P. Wendlandt, *Catalytic conversion of silicon tetrachloride to trichlorosilane*, *J. Chem. Soc., Faraday Trans.* 89 (1993) 1085–1087.
- [23] W.M. Ingle, M.S. Peffley, *Kinetics of the hydrogenation of silicon tetrachloride*, *J. Electrochem. Soc.* 132 (1985) 1236–1240.
- [24] A.V. Gusev, R.A. Kornev, A.Y. Sukhanov, *Behavior of carbon-containing impurities during plasma synthesis of trichlorosilane*, *High Energ. Chem.* 42 (2008) 56–58.
- [25] A.V. Gusev, R.A. Kornev, A.Y. Sukhanov, *Preparation of trichlorosilane by plasma hydrogenation of silicon tetrachloride*, *Inorg. Mater.* 42 (2006) 1023–1026.
- [26] A.V. Vorotyntsev, S.V. Zelentsov, V.M. Vorotyntsev, et al., *Quantum-chemical simulation of the dissociative chemisorption of hydrogen on metal surfaces of nanoclusters*, *Russ. Chem. Bull.* 64 (4) (2015) 759–765.
- [27] A.V. Vorotyntsev, S.V. Zelentsov, V.M. Vorotyntsev, *Quantum-chemical simulation of silicon tetrachloride hydrogenation*, *Russ. Chem. Bull.* 60 (8) (2011) 1531–1536.
- [28] V.M. Vorotyntsev, P.N. Drozdov, I.V. Vorotyntsev, I.V. *High purification of substances by a gas separation method*, *Desalination* 240 (2009) 301–305.
- [29] K.A. Burlov'shakov, *Khimiya i tekhnologiya redkikh i rasseyannyykh elementov. V 2 chastyakh (Chemistry and Technology of Rare and Scattered Elements, in 2 parts)*, Moscow: Vysshaya shkola, 1976, part 1.
- [30] A.F. Zhigach, D.S. Stasinevich, *Khimiya gidridov (Chemistry of Hydrides)*, Leningrad: Khimiya (1969); 676.
- [31] V.M. Vorotyntsev, P.N. Drozdov, I.V. Vorotyntsev, K.Y. Smirnov, *Germane high purification by membrane gas separation*, *Desalination* 200 (2006) 232–233.
- [32] G.G. Devyatykh, A.D. Zorin, A.D. *Letuchie neorganicheskie gidridy osoboi chistoty (Special-Purity Volatile Inorganic Hydrides)*, Nauka, Moscow, 1974, pp. 207.
- [33] EP. Patent 1654400, Method for preparing high-purity germanium hydride, 2006.
- [34] WO. Patent 2005005673, Method for preparing high-purity germanium hydride, 2005.
- [35] CN. Patent 1820093A, Method for preparing high-purity germanium hydride, 2006.
- [36] V.M. Vorotyntsev, G.M. Mochalov, A.K. Matveev, A.V. Malyshev, I.V. Vorotyntsev, *Determination of Trace Impurities of H_2 , O_2 , Ar, N_2 , CO, CO_2 , and Hydrocarbons in High-Purity Monosilane by Gas Chromatography*, *J. Anal. Chem.* 58 (2) (2003) 156–159.
- [37] V.M. Vorotyntsev, G.M. Mochalov, S.S. Suvorov, A.O. Shishkin, *Gas-chromatographic determination of the impurity composition of permanent gases, methane, carbon monoxide, and carbon dioxide in high-purity monogermane*, *J. Anal. Chem.* 65 (6) (2010) 634–639.
- [38] A.V. Kadamtsava, A.V. Vorotyntsev, V.M. Vorotyntsev, A.N. Petukhov, A.M. Ob'edkov, K.V. Kremlev, B.S. Kaverin, *Effect of the catalytic system based on multi-walled carbon nanotubes modified with copper nanoparticles on the kinetics of catalytic reduction of germanium tetrachloride by hydrogen*, *Russ. J. Appl. Chem.* 88 (4) (2015) 595–602.
- [39] A.V. Vorotyntsev, G.M. Mochalov, V.M. Vorotyntsev, *Kinetics of catalytic hydrogen reduction of SiCl_4 in the presence of nickel chloride*, *Inorg. Mater.* 49 (1) (2013) 1–5.
- [40] B. Brady L.R. Martin T. Moore *Reaction Mechanism and Modeling of SiCl_4 Combustion* Aerospace Report No. ATR-2003 (8136)-5, 2016 9.
- [41] L.A. Mochalov, R.A. Kornev, A.V. Nezhdanov, et al., *Plasma Chem. Plasma Process.* 36 (3) (2016) 849–856.